Letters to the Editor

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ON THE ULTRAVIOLET ABSORPTION SPECTRA OF ORTHO AND META FLUOROBENZONITRILES

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The electronic absorption spectra in vapour phase give information in detail about the vibrational frequencies of excited electronic states of free molecules. With this aim, the absorption spectra of ortho- and meta-fluorobenzonitriles in vapour phase were photographed for the first time on the Hilger medium and large quartz spectrographs in the quartz ultraviolet region. The absorption cells used in the investigation were varied from 10 to 150 cms over a temperature range of 0° to 80°C. The present short communication reports the 0, 0 bands, the ground and excited states fundamental frequencies and some low lying vibrations of these molecules.

If we assume – CN group as one atom, both these molecules can be considered to belong to C_s point group, with molecular plane as the only element of symmetry. The region of the absorption spectrum in each case suggests that the electronic transition in question corresponds to $A_{1g} \rightarrow B_{2u}$ forbidden transition of benzene. This transition of benzene becomes allowed $A' \rightarrow A'$ in C_s point group, with the transition moment lying in the molecular plane.

ortho-fluorobenzonitrile: The absorption spectrum lies in the region 2890-2590 Å. The strong band appearing at 36034 cm^{-1} has been identified as the 0, 0 band of the system. Obviously, the bands with separations 143, 366, 457, 598, 732, 848, 1039, 1163 and 1257 cm^{-1} from the 0, 0 band towards the longer wavelenth side have been assigned as the fundamentals of the ground electronic state. Strong bands with separation 118, 340, 496, 667, 691, 815, 947, 1174, 1256 and 1423 cm^{-1} from the 0, 0 band towards the shorter wavelength side have been chosen to represent fundamentals of the excited electronic state. The remaining

bands of the system have been explained as combinations and overtones of these fundamental vibrations. The ground state fundamental frequencies are found quite in agreement with the infrared values (Singh, Notable bands at separations of 29, 41, 57 and 91 cm^{-1} on the red of most of the strong bands have also been observed.

meta-fluorobenzonitrile: The discrete red degraded absorption bands are found to occur in the region 2890-2560 Å. The intense band at 35992 cm^{-1} has been identified as the 0, 0 band of the system. The interpretation of the bands has been suggested in terms of ground state frequencies—142, 456, 585, 746, 855, 1012, 1166 and 1278 cm^{-1} and excited state frequencies—102, 402, 471, 658, 688, 972, 1141 and 1269 cm^{-1}. It may be remarked that at 80°C the vapour pressures of the isomers will be about 30 times the value at 0°C. This has enabled observation of the ground state frequencies of the order of 1250 cm^{-1}. Several progressions of symmetric vibrations and many combinations between them have been observed. The ground state fundamental vibrations observed are in agreement with the normal vibrations observed in infrared absorption (Singh.). Many strong bands are accompanied by strong components at separations of 27, 40, 49 and 62 cm^{-1} on their red side. These have been interpreted as due to $v-v$ transitions.

The selection of above fundamental vibrations in the ground and excited states is on the basis of their intensities, their correlation with infrared frequencies and their combinability with other chosen frequencies. Further, their correctness has been justified by correlating them with the normal vibrations of other mono-substituted benzonitriles (Varadarajan; Padhye *et al*, 1962; Pandey *et al*, 1966; Singh *et al*, 1965; Pathak, 1967; Cooper, 1953).

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